Size Effects of Ultrafine PtRu Particles on the Oxidation of Methanol in H_2SO_4

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Although the design of active anodes is an important subject for the development of polymer electrolyte membrane fuel cells, the effect of the size of PtRu particles on the electrocatalytic oxidation of methanol; *i.e.*, the "size effects", is still unclear. We have studied the size effects for the electrochemical oxidation of methanol with $Pt_{50}Ru_{50}$/C/GC (C: Vulcan XC72R; 254 $m^2\ g^{-1}$) catalyst electrodes.[1,2] In the present investigation, various carbon black supports with different surface area have been used for the catalyst preparation to reveal the size effects more clearly.

The $Pt_{50}Ru_{50}$/C catalyst powders were prepared by an impregnation method with carbon black (29-800 $m^2\ g^{-1}$) and ethanolic solutions of $Pt(NO_2)_2(NH_3)_2$ and $RuNO(NO_3)_x$. The alloy composition used was $Pt_{50}Ru_{50}$, (Pt : Ru = 1 : 1 in mole), because this composition was the most active in the binary alloy catalyst system. The decomposition of the metal complexes supported on the carbon black powder was conducted in a stream of H_2 + N_2 at 450°C. The catalytic activity for the oxidation of methanol decreased with increase in the preparation temperature from 200 to 450°C. The surface area of the metal particles was determined by cyclic voltammetry with the amount of electricity used for the oxidation of pre-adsorbed CO. The catalyst electrodes for the examination of the electrocatalytic activity was prepared with a glassy carbon rod (5 mm in diam.) on which about 0.10 mg of the catalyst powder $Pt_{50}Ru_{50}$/C was fixed with a dispersion of Nafion®.[3] The catalytic activity of the electrodes was determined by chronoamperometry. The dispersion state of the PtRu particles on carbon black was observed with high-resolution scanning electron microscope (Hitachi 5000).

The extent of alloying of PtRu particles seems to affected by the preparation temperature, surface area carbon black support, and loading amount of $Pt_{50}Ru50$, revealed by X-ray diffraction analysis. Both the specif activity, i_{sp} (current density per real surface area, units in m^{-2}), and mass activity, i_{mass} (current density per loadi amount, units in A g^{-1}), of $Pt_{50}Ru_{50}$ particles for t oxidation of methanol at 60°C in 0.5 M H_2SO_4 have be found to decrease with a decrease in the size of the me particles for almost all $Pt_{50}Ru_{50}$/C(carbon black) catalys examined.

In order to clarify the origin of the "size effects" found this investigation, the electronic structure and surface all composition of the PtRu particles as well as the surfa species of OH_{ad}, CO_{ad} and CHO_{ad} should be characterize although such information concerns only the overa properties of the alloy catalysts.

References

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